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A Theory of Magnets with Competing Double Exchange and Superexchange Interactions

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We study the competition between ferromagnetic double exchange (DE) and nearest-neighbour antiferromagnetic exchange in CMR materials. Towards this end, a single site mean field theory is proposed which emphasizes the hopping-mediated nature of the DE contribution. We find that the competition between these two exchange interactions leads to ferro- or antiferromagnetic order with incomplete saturation of the (sub)lattice magnetization. This conclusion is in contrast to previous results in the literature which find a canted spin arrangement under similar circumstances. We attribute this difference to the highly anisotropic exchange interactions used elsewhere. The associated experimental implications are discussed.

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The colossal magnetoresistance (CMR) manganese oxides have received considerable attention recently [1] . In the CMR regime, these materials exhibit ferromagnetism which is generally believed to result from a conduction electron-mediated double exchange (DE) mechanism [2]. In addition, there exists evidence which suggests [3,4] the presence of an antiferromagnetic superexchange of comparable scale. Thus, a full understanding of the magnetic order in the CMR materials requires a treatment of the competition between ferro- and antiferromagnetic interactions. The aim of the present paper is to address this competition and, by doing so, revisit earlier claims in the literature [5] which suggest that spin canting may be the most natural means of accommodating these two opposing interactions.

In the literature, previous related calculations [5] have been performed for a strongly anisotropic model in which the inter- and intra-layer direct exchange constants have different signs [6]. In this paper it is assumed that direct interactions have everywhere the same (antiferromagnetic) sign and magnitude. This is viewed as more appropriate for the $La_{1-x}Ca_xMnO_3$ perovskite family away from the x=0 endpoint, as well as for the layered manganates such as $La_{2-2x}Sr_{1+2x}Mn_2O_7$. In view of the considerable interest in these layered systems [3,4,7], the present calculations address primarily the two dimensional (2D) lattice; nevertheless, our 2D results are qualitatively representative of the three dimensional case as well. In the present situation, there are no ferromagnetically locked layers; in this way spin fluctuations are enhanced, thereby leading to stronger fluctuations in the electronic kinetic energy. Because these fluctuations are not fully captured by lowest order (i.e., Hartree–Fock like) treatments, in the present paper we introduce a new approach to the problem.

The present theoretical framework is based on a single site mean field theory which emphasizes the hopping-mediated nature of the DE-induced ferromagnetic interaction. This is to be contrasted with alternative approaches in the literature [5,8] which implicitly introduce a Heisenberg-like exchange interaction to represent these DE effects. Our starting point is the standard Hamiltonian [5,9] derived for the case of infinite Hund's rule coupling:

$$\mathcal{H} = -t_0 \sum_{<i,j>} \cos\frac{\theta_{ij}}{2} \{c_i^\dagger c_j + c_j^\dagger c_i\} + \frac{J_{AF}}{S^2} \sum_{<i,j>} \vec{S}_i \cdot \vec{S}_j - \frac{H}{S} \sum_i S_i^z \,. \quad (1)$$

Here c_j annihilates a fermion on site j, $\vec{S}_i$ represents a classical core (localized) spin ($S \gg 1$), J_{AF} is the nearest-neighbour antiferromagnetic exchange integral, H – external field, and $\cos\theta_{ij} = \vec{S}_i \cdot \vec{S}_j / S^2$. Throughout this paper, we use units in which the bare hopping t_0, $\hbar$, k_B, μ_B, and the lattice period are equal to unity. In the first term of Eqn. (1), we have omitted Berry phase effects which are insignificant for a single-site mean field treatment.

The random distribution of localized spins leads in Eqn. (1) to a highly disordered electronic hopping problem. In our mean field approach we focus on a central site characterized by hopping b to the surrounding sites. This site is embedded in a medium with average hopping t, $t \neq b$ [10]; for clarity these parameters are indicated schematically in Fig. 1. The quantities b and t depend in a self consistent fashion on the change, $\delta\Omega$, in the free energy, associated with the change in hopping matrix elements $t \to b$. This kinetic energy contribution to $\delta\Omega$, which can be evaluated following Ref. [11], is given by

$$\delta\Omega_{DE}(b,t,T) = \int f(\epsilon)\xi(\epsilon)d\epsilon \quad (2)$$

$$+\theta(b-t)\cdot(\varphi(z_0)-\varphi(-Dt))\ ,$$

where the spectral shift function $\xi(\epsilon)$ is given by

$$\pi \mathrm{ctg}\pi\xi(\epsilon) = -\frac{1}{\epsilon\nu(\epsilon)}\frac{b^2}{t^2-b^2} - \frac{1}{\nu(\epsilon)}\mathcal{P}\int\frac{\nu(\eta)d\eta}{\epsilon-\eta}\,, \quad (3)$$

the bound state energy $z_0 < -Dt$ is the root of

$$1+\frac{t^2-b^2}{t^2}\left\{-1+z\int\frac{\nu(\eta)d\eta}{z-\eta}\right\}=0\,, \quad (4)$$

$\nu(\epsilon)$ is the density of states, $\varphi(z) = -T\ln\{1+\exp[(\mu - z)/T]\}$, μ is the chemical potential, and $f(z) = \{\exp[(z-\mu)/T]+1\}^{-1}$. Eqns. (2–4) are valid for a simple lattice in any dimensionality D from 1 to 3; the energy integrations are performed over the entire conduction band, extending from $-Dt$ to Dt. It should be stressed, that it is because of the locality of the perturbation (which represents a lattice analogue of an s-wave scattering problem) that the quantity $\delta\Omega$ can be evaluated *exactly* [11].

In the ferromagnetic phase at $T > 0$, the net energy cost of a single-spin fluctuation is (in $2D$) given by

$$\delta\Omega_1 = \delta\Omega_{DE}(b_1,t,T) + 4J_{AF}\langle\cos\theta_{12}\rangle_2 - H\cos\alpha_1\ - \\ -4J_{AF}\langle\cos\theta_{12}\rangle_{12} + H\langle\cos\alpha_1\rangle_1\,. \quad (5)$$

Here, θ_{12} is the angle formed by the fluctuating spin $\vec{S_1}$ with a neighbouring spin $\vec{S_2}$, and α_1 is the angle between $\vec{S_1}$ and the average magnetization, $\vec{M}$ (see Fig. 1). We use the notation $\langle ...\rangle_l$ to represent averaging over the Boltzmann probability distribution of spin $\vec{S_l}$, $w_l \propto \exp(-\delta\Omega_l/T)$. It follows that $\langle\cos\theta_{12}\rangle_2 = M\cos\alpha_1$, and

$$b_1^2 \equiv \langle\cos^2(\theta_{12}/2)\rangle_2 = (1+M\cos\alpha_1)/2\,, \\ t^2 \equiv \langle b_1^2\rangle_1 = (1+M^2)/2\,. \quad (6)$$

The central mean field equation of our formalism is given by $M = \langle\cos\alpha_1\rangle_1$.

In the ferro- and antiferromagnetic phases, it is useful to construct a reference framework with which to compare our results. We define $J_{eff}(M)$ which represents an effective M- dependent exchange constant for a Heisenberg-like magnet. The appropriate exchange constant can be deduced by considering small spin fluctuations ($|\cos\alpha - M| \ll 1$), which correspond to small fluctuations in the hopping matrix elements ($|t-b| \ll t$). A perturbation expansion of Eqn. (2), then leads to

$$\delta\Omega_{DE}(b,t,T) \approx -2\frac{t-b}{t}\int\epsilon f(\epsilon)\nu(\epsilon)d\epsilon = 2(t-b)|E_0|\,, \quad (7)$$

at leading order in T/t, where E_0 is the kinetic energy of the carriers for $t = 1$. In the ferromagnetic state, it follows from Eqn. (7) that

$$J_{eff}(M) = J_{AF} - \frac{1}{8}|E_0|\cdot\sqrt{\frac{2}{1+M^2}}\,. \quad (8)$$

The second term in the above equation represents the DE contribution. This term, which is contained in other mean field schemes [8,12], increases as M decreases. As a consequence, for moderately strong antiferromagnetic exchange interactions $J_{eff}(M)$ changes sign as M varies from 0 to 1. This behaviour has important consequences: it leads to a lack of saturation in the low temperature magnetization. Typical results for $M(T)$ are plotted in Fig. 2 for these moderately strong exchange interactions ($|E_0| + 2H < 8J_{AF} < \sqrt{2}|E_0| + 2H$). Here the solid line represents the full calculation, while the dashed line is obtained using the effective exchange interaction. For comparison we plot (dotted line) the magnetization of a conventional Heisenberg magnet with the same T_C.

The lack of saturation seen in Fig. 2 can be understood as follows. As T decreases, the magnitude of single spin fluctuations also decreases. This leads to an increase of M, which in turn implies a decrease in $|J_{eff}|$ (and thereby a tendency to *decrease* M). Thus, through this self-adjustment of the effective exchange interaction (which never becomes large in comparison with T), the magnetization fails to reach its proper saturation value, $M_0 = 1$ [13]. These self consistent changes in $|J_{eff}|$ lead to inadequacies of the effective exchange approximation at low T. As may be seen in Fig. 2, the behaviour obtained in this approximation differs significantly from that found using the full calculation of $M(T)$. This difference is due to the fact that when $J_{eff} \lesssim T$ is small, quadratic terms (in $(t-b)/t$) dominate the physics [14].

The Néel antiferromagnetic state (of the metallic phase) can be treated similarly [15]. It can be shown that Néel ordering (which arises for $J_{AF} > 2^{-5/2}|E_0|$ in zero field), always exhibits undersaturation of the sublattice magnetization. This undersaturation (which leads to a finite bandwidth) may be viewed as consistent with the presumed metallic state.

Our discussion thus far has not included the canted phase first proposed by De Gennes [5]. This phase is characterized by spin ordering with two equal sub-lattice magnetizations m which form an angle 2γ between them. In the present model, spin canting requires the presence of a magnetic field to break the high degeneracy which would otherwise occur. This degeneracy is related to the fact that the energy of the system depends solely on the cosine of the angle which the spin $\vec{S_1}$ (of sublattice I) forms with its nearest neighbours belonging to sublattice II. In the context of single site mean field approaches, this energy does not change as the spin $\vec{S_1}$ moves along any cone around the average direction of spins of sublattice II. Thus, on average the spin $\vec{S_1}$ will be aligned with sublattice II, rather than I. Therefore, in the absence of perturbations (caused by next-nearest-neighbour exchange, anisotropy effects, quantum corrections, or small

external fields) the canted state is destabilized. Since the underlying degeneracy is site-local [16], its effects will be suppressed only when the energy scale of a perturbation *per individual spin* is comparable with that of the thermal motion of a *single* spin, that is, with the temperature T.

To characterize the finite field canted state, we use the full non-perturbative expression (2), with appropriate modifications to Eqns. (5– 6) [17]. We obtain two coupled self consistent equations, one for the component of $\langle \vec{S}_1 \rangle$ parallel to the magnetization of sublattice I,

$$-\sin 2\gamma \, \langle \sin\alpha_1 \, \cos\beta_1 \rangle_1 + \cos 2\gamma \, \langle \cos\alpha_1 \rangle_1 = m \,, \qquad (9)$$

and another for the perpendicular component,

$$\cos 2\gamma \, \langle \sin\alpha_1 \, \cos\beta_1 \rangle_1 + \sin 2\gamma \, \langle \cos\alpha_1 \rangle_1 = 0 \,. \qquad (10)$$

where α_1 and β_1 are polar and azimuthal angles of the spin $\vec{S}_1$ measured with respect to the co-ordinate system that has, as its polar axis, the average direction of the spins of sublattice II. We choose $\beta_1 = 0$ for the spin $\vec{S}_1$ lying within the plane containing the two sublattice magnetizations.

The low-T canted state is found to be stable for $8J_{AF} > |E_0| + H$. The solutions of Eqns. (9–10) for typical parameters are illustrated in the inset of Fig. 2. One can see that, as $T \to 0$ in the canted phase, the sublattice magnetization m approaches its proper saturation value $m = 1$. Note that the ferromagnetic ($\gamma = 0$) solution to the mean field equations is present at $H > 0$ as well. In Fig. 2 (inset), the corresponding magnetization, $M_{FM}(T)$, is represented by the dotted line. However, when the canted ($\gamma > 0$) solution exists, it corresponds to a lower value of the free energy. The canted solution branches from the ferromagnetic one at temperature $T \sim H$; at this point the undersaturated ferromagnetic state undergoes a second-order spin-flip transition into the low temperature canted state [18]. This lends support to the notion that undersaturation is characteristic of the generic low temperature regime [19].

Typical phase diagrams for the DE–superexchange magnet in (left) zero and (right) non-zero field are presented in Fig. 3. For t_0 of the order of an eV, our choice of parameters corresponds to reasonable values of $J_{AF} \lesssim 300$K. In zero field (left), the solid line represents the phase boundary between paramagnetic (PM) and antiferro- (AFM) or ferromagnetic (FM) metallic phases. The ordered phases are undersaturated at low T (for slightly smaller J_{AF} we find a critical value of bandfilling, x_1, which divides the saturated, $x > x_1$, and undersaturated regimes). At low temperatures and small concentrations (in 2D, $x < 0.215$), the undersaturated AFM state becomes thermodynamically unstable ($\partial\mu/\partial x < 0$), signalling either the onset of a more complicated spin arrangement or phase separation. The dashed line in Fig. 3 corresponds to the boundary of this region ($\partial\mu/\partial x = 0$).

The right panel in Fig. 3 shows that in the presence of a magnetic field the PM–FM transition is replaced by a smooth crossover (dotted line). The spin arrangement of the AFM phase becomes non-collinear (flop-phase), and has the same symmetry properties as the canted phase (CM), which becomes stable at lower T (replacing the $H = 0$ undersaturated FM and AFM phases). The two are separated from the PM and FM region by a second-order phase transition, which is represented by the solid line. At sufficiently small x the latter approaches the $H = 0$ Néel transition line. The thermodynamic instability line (not shown) is only slightly affected by H.

These calculations have made a number of predictions which can be tested experimentally. The layered materials $La_{2-2x}Sr_{1+2x}Mn_2O_7$, with $x = 0.4$, presumably lie either within the region where the system should display undersaturated ferromagnetic behaviour at low T, or on the brink of this region, where thermal fluctuations should still be stronger than in a conventional magnet. Some measurements of the absolute value of magnetization in $x = 0.4$ samples support undersaturation [20,21], while others do not [22]. We also note that the presence of undersaturation in ferro- and antiferromagnetic phases may well signal that in reality the system favours more complicated (*e.g.* spin glass-like, cf. Ref. [22]) spin ordering, that cannot be addressed within a single-site mean field theory.

It is natural to expect that the relative strength of the superexchange interaction is even higher in $x = 0.3$ compounds, so that this compound may be suitable for observing canting under the proper field and temperature conditions: $T \lesssim H$, although experiments have not yet been performed in this regime. There have been no observations of an *ordered* canted state (as distinguished from possible canting correlations reported in Ref. [4]) in the layered compounds. This is consistent with our results. Finally, we propose that the magnetization dependence of the effective exchange constant (available through spin wave measurements) should be studied in both 3D and 2D systems.

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[13] Instead, the limiting value of the zero field, zero temperature magnetization is given by $M_0 = \{(E_0/J_{AF})^2/32 - 1\}^{1/2} < 1$.
[14] Within the effective exchange approximation, strong fluctuations of *both* angular co-ordinates of each spin persist at low T. By contrast, the full calculation shows that the fluctuations of the polar angle freeze out, $\cos\alpha_i \to M_0$.
[15] In this case, $\langle\cos\theta_{12}\rangle_2 = -m\cos\alpha_1$, where m is sublattice magnetization and α_1 is the angle formed by the spin $\vec{S}_1$ with its average direction. Eqns. (6) are replaced by $b_1^2 = (1 - m\cos\alpha_1)/2$ and $t = (1 - m^2)/2$. Instead of (8) we obtain $J_{eff}(m) = J_{AF} - |E_0|\{2/(1 - m^2)\}^{1/2}/8$.
[16] Another example of a classical spin system with site-local continuous degeneracy is provided by the Kagomé antiferromagnet.
[17] Instead of Eqns. (5–6), we obtain $\delta\Omega_1 = \delta\Omega_{DE}(b_1, t, T) + 4J_{AF}m\cos\alpha_1 - H(-\sin\gamma\,\sin\alpha_1\,\cos\beta_1 + \cos\gamma\cos\alpha_1)$, $b_1^2 = (1 + m\cos\alpha_1)/2$, and $t^2 = (1 + m^2\cos 2\gamma)/2$.
[18] The spin-flop phase of the undersaturated antiferromagnet evolves into the canted state via a smooth crossover at $H \sim T$.
[19] While it is not clear whether undersaturation is present in the case of quantum spins, we note that this would be not inconsistent with the results obtained for the somewhat similar case of quantum ferrimagnets (see: A. V. Chubukov *et al.*, J. Phys.: Cond. Matt. **3**, 2665 (1991)).
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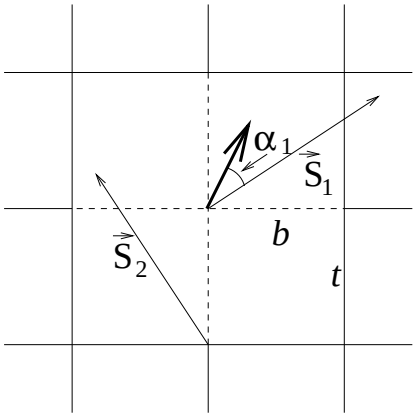
FIG. 1. Single-spin fluctuation in the ferromagnetic phase. The bold arrow represents the average magnetization, and the dashed lines correspond to the hopping amplitude b, which differs from the background hopping value t (solid lines).

FIG. 2. Magnetization vs. temperature in the ferromagnetic phase at $H = 0$, $x = 0.4$, and $J_{AF} = 0.06$. The solid, dashed, and dotted lines correspond to the 2D DE– superexchange magnet, effective exchange approximation, and usual Heisenberg ferromagnet, respectively. The inset shows the behaviour of the sublattice (solid line) and net (dashed line, $M = m\cos\gamma$) magnetizations in the canted state at $H = 0.01$ in comparison with the magnetization of the ferromagnetic state (dotted line).

FIG. 3. Phase diagrams of the DE–superexchange magnet for $J_{AF} = 0.06$ at $H = 0$ (left panel) and $H = 0.01$ (right panel), showing the ferro-, antiferro- (flop-phase at $H > 0$), paramagnetic, and canted phases (FM, AFM, PM, and CM, respectively). The behaviour of the system is symmetric with respect to quarter-filling, $x = 0.5$.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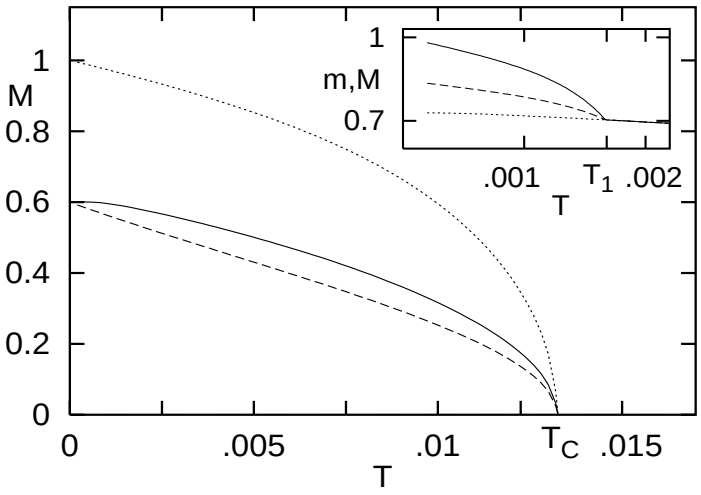
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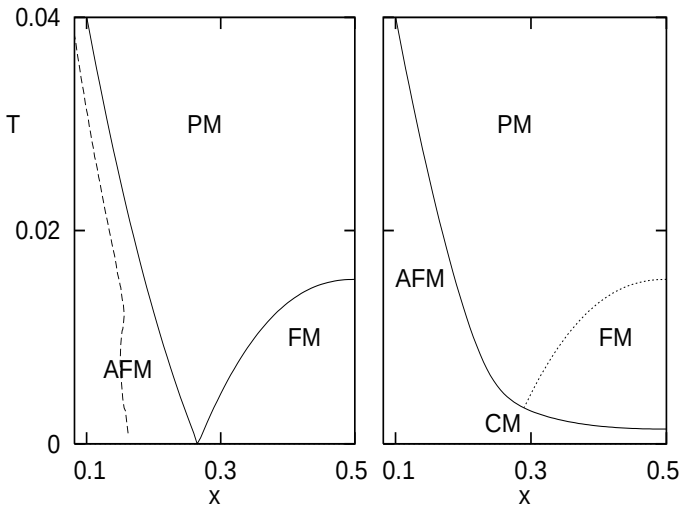
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